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$Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$: A Novel Type of SOFC Cathode

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The fabrication and electrochemical activity of a type of solid oxide fuel cell (SOFC) cathode is described in this paper. In search of new cathodes a $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ compound was synthesized using the glycine-nitrate method. It turned out that this was a two-phase compound consisting of two perovskite phases, a cubic and an orthorhombic phase, as shown by Rietveld refinements. These two phases were synthesized and a cone-shaped electrode study was undertaken. It was shown that the composite cathode had an electrochemical activity superior to that of the two single-phase perovskites, indicating that the unique microstructure of this type of cathode is essential for achieving high electrochemical activity toward the reduction of oxygen in a SOFC.
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Currently a large research effort is being carried out to lower the operation temperature of solid oxide fuel cells (SOFCs). Among the hurdles one must pass is the development of a cathode with a higher electrochemical activity than that of the classical strontium-substituted lanthanum manganite (LSM)/yttria-stabilized zirconia (YSZ) composite cathode. One commonly used cathode is a composite of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ with $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO10). However, in the low-temperature limit of 550–600°C the electrochemical activity of this cathode is still too low for practical applications, and new cathode materials and structures must therefore be developed. Such cathodes could be Gd-containing Fe–Co-based perovskites. To our knowledge, the first example of the use of Gd-containing perovskites as cathodes in a SOFC were reported by Tu et al.[1] In their study they investigated Fe–Co-based perovskites containing La, Pr, Nd, Sm, or Gd. Here the Nd-containing perovskite showed the highest activity and the Gd-containing perovskite a rather low activity. No comments were made on the presence of two-phase structures. Riza et al.[2] synthesized Fe–Co-based perovskites with La, Pr, Nd, Sm, Eu, or Gd. It was shown that most of the perovskites were two-phase systems with the secondary phase being Co_3O_4. Later, Qiu et al.[3] investigated Fe–Co-based perovskites with Pr, Nd, or Gd as A-site cations (together with Sr) as cathodes in a SOFC. They suggested that single-phase materials were formed during synthesis. The best electrochemical activity was achieved using the Pr-containing materials. The electrochemical activity for the reduction of oxygen in a SOFC of yet another series of Fe–Co-based perovskites was investigated by Qao et al.[4] Using the A-site cations Ce, Gd, Sm, or Dy they showed that the Dy-containing perovskite showed superior activity. The materials were all claimed to be of single phase.

Different cathode materials were investigated by Ralph et al.[5] They showed that Co-based perovskites with either Gd or Pr as A-site cations together with Sr revealed the best electrochemical activity. No comments on multiphase systems were made. Dyck et al.[6] has recently shown that $Gd_{0.8}Sr_{0.2}Fe_{1-y}Co_yO_{3-\delta}$ is a two-phase system using powder X-ray diffraction (XRD) and Rietveld refinement. The powders contain an orthorhombic perovskite phase and a cubic perovskite phase. However, the authors did not show scanning electron microscopy (SEM) images, nor was energy-dispersive X-ray spectroscopy (EDS) analysis carried out to determine the composition of the two individual perovskite phases. Kammer[7] found that a Gd-containing Fe–Co-based perovskite had a activity toward the reduction of oxygen superior to Fe–Co-based perovskites with larger A-site cations. It was also shown by XRD and SEM that the Gd-containing Fe–Co-based perovskite was a two-phase compound. It was suggested that the superior activity toward the reduction of oxygen was due to the formation of the two-phase structure. However, the electrochemical activity of the individual phases was not determined.

This is a combined powder XRD, SEM, EDS, and cone-shaped electrode study of the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$. The use of cone-shaped electrodes were originally brought forward by Fabry and Kleitz.[8] The benefit is that one elucidates the effect of microstructure on the activity of the electrodes. Also, no reaction layer is formed between the electrode and the electrolyte during processing of the electrodes. Further, the cone-shaped electrode setup has a simple geometry which makes it possible to estimate the contact area of the cone-shaped electrode.

Experimental

Powders of the perovskites were made by the glycine-nitrate combustion route.[9] In general the metal-nitrate solutions were mixed in the appropriate ratio in a beaker, and glycine was then added to the solution. The solutions were then heated on a hot plate until they ignited. Finally, the powders were calcined at 1100°C/12 h. The following nitrates were used: $Gd(NO_3)_3$ (Alfa Aesar, 99.9%), $Sr(NO_3)_2$ (Alfa Aesar, 99%), $Fe(NO_3)_3$ (Alfa Aesar, 98%), and $Co(NO_3)_2$ (Alfa Aesar, 99.8%). Powder XRD was then performed to evaluate the purity of the synthesized compounds using a Stoe powder diffractometer with Cu Kα radiation. The cylinders for fabrication of the cone-shaped electrodes were made by pressing the powders in an appropriate die and sintering at 1250°C/12 h. The density of the cylinders after sintering was determined by the Archimedes method. The density of the cylinders was more than 90% of the theoretical value. Cones for the electrochemical measurements were made by machining the cylinders with diamante tools. As an electrolyte a pellet of CGO10 (Rhodia) was used. The CGO10 pellet was fabricated as follows. The CGO10 powder was mixed with stearic acid and glycerine in a ball mill with EtOH overnight. The mixture was dried before being pressed in a die. The pellet was sintered at 1500°C/2 h. As a counter/reference electrode a silver electrode was used. Silver was as added as a paste (Engelhard) and was sintered in situ at 800°C. For the electrochemical measurements a Solartron 1260 gain-phase analyzer was used. Electrochemical impedance spectroscopy (EIS) was recorded in the frequency range of 1 MHz to 0.05 Hz, with five points measured at each decade. An amplitude of 24 mV was used throughout. The measurements were performed at 800, 700, and 600°C, starting at the highest temperature. Before the recording of the data, the sample was equilibrated at a given temperature for 24 h. The measurements on the cone-shaped electrodes were done in a setup described in Ref. 10. The data obtained by EIS were treated in the PC-DOS program Equivert.[11] From the intercept with the real axis at high frequency, R_s, the contact area was determined using Newman's formula[12]

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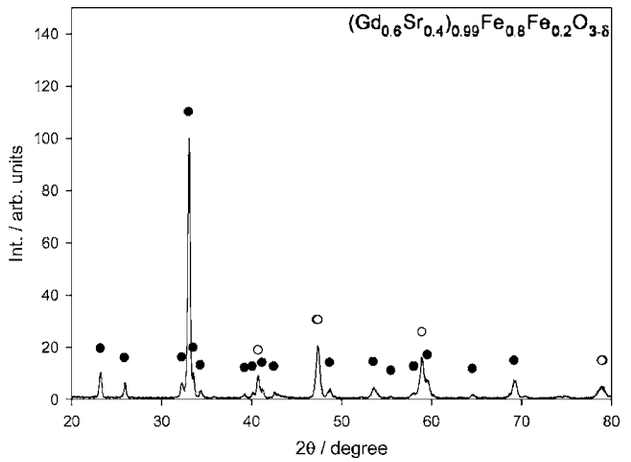

Figure 1. Powder XRD diffractogram of the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ recorded in air at room temperature. Peaks originating from the orthorhombic phase are marked with a solid circle and peaks originating from the cubic phase are shown with an open circle where they deviated from the orthorhombic phase.

$$r = \frac{1}{4R_s\sigma^*}$$

where σ^* is the specific conductivity of the electrolyte. The microstructure of the cone-shaped electrodes was investigated using a JEOL JSM-840 scanning electron microscope.

Results and Discussion

The powder XRD pattern of the powders with composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ is depicted in Fig. 1. It is seen that the $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ compound is a two-phase system, one orthorhombic and one cubic perovskite phase. The lattice parameters of the two phases from Rietveld refinement are given in Table I. The electrochemical activity of the cone-shaped electrode is shown in Fig. 2, where the area specific resistance (ASR) is plotted vs reciprocal temperature. The ASR at 600°C of this cone-shaped cathode material is very low, 0.89 Ω cm^2 at 600°C. This is among the lowest values measured on a cone-shaped electrode.[7,13-16] The activation energy is 121 kJ/mol. In Fig. 3 the impedance spectrum recorded at 800°C can be found. It is seen that this spectrum consists of two arcs. A SEM micrograph of the cone with the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ is given in Fig. 4. The cone has a unique microstructure where one phase has a small particle size (orthorhombic) and the other phase a relative large particle size (cubic). Using EDS the composition of the two phases was determined to be $Gd_{0.49}Sr_{0.51}Fe_{0.79}Co_{0.24}O_{3-\delta}$ (orthorhombic) and $Gd_{0.76}Sr_{0.24}Fe_{0.75}Co_{0.22}O_{3-\delta}$ (cubic). The assignments of the crystal structure of the two individual phases were done by synthesizing the two compounds found from EDS and determining their XRD powder patterns. The composition of these two phases most likely depends on the sintering temperature and oxygen partial pressure. In order to evaluate the electrochemical activity of the two individual phases, synthesis of these phases was made. The attempt to make these two phases resulted in single-phase materials as determined by powder XRD. The lattice constants of the two compounds can be found in Table I and the powder patterns can be found in Fig. 5. After the synthesis of these two phases the electrochemical activity of the two phases were evaluated using the cone-shaped electrode technique. The electrochemical activity of these two phases indi-

Table I. Lattice constants of the synthesized perovskite phases.

	Two-phase compound (Å)	Cubic phase (Å)	Orthorhombic phase (Å)
A	7.630		7.617
B	5.559		5.512
C	5.334		5.322
A'	3.832	3.836	

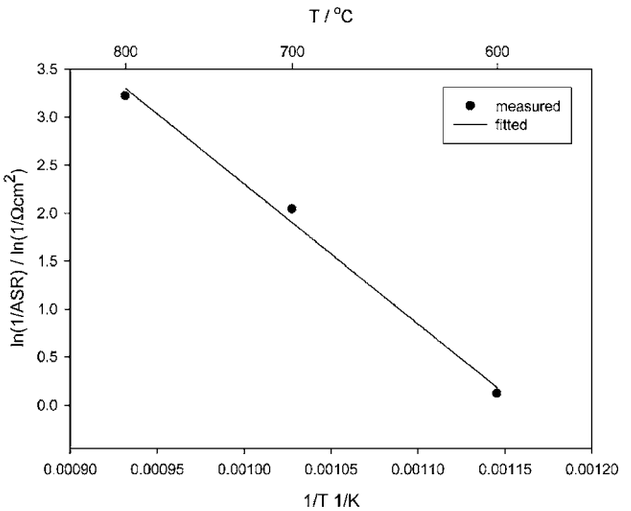

Figure 2. Activation energy plot for the $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ cone-shaped composite cathode in the temperature range 600–800°C.

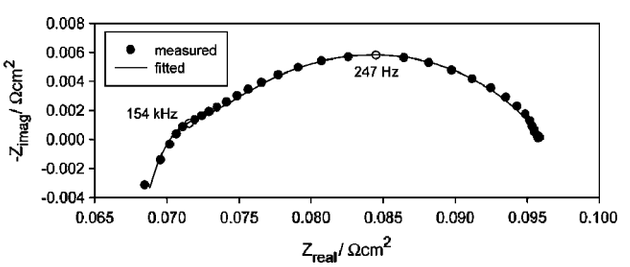

Figure 3. EIS spectrum of a $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ cathode measured at 800°C in air. The spectrum was fitted with the circuit $LR_s(R_1Q_1)(R_2Q_2)$. The calculated spectrum is shown with a solid line.

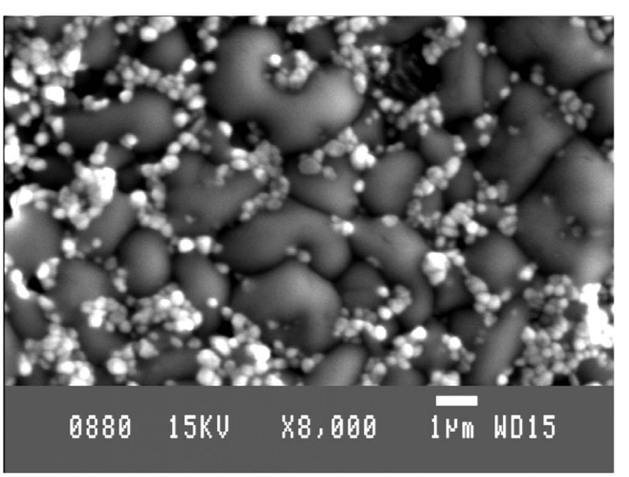

Figure 4. SEM micrograph of the $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ composite cone-shaped cathode.

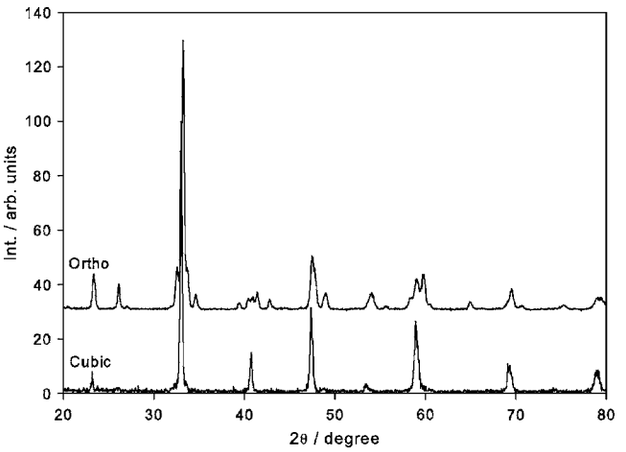

Figure 5. Powder XRD diffractograms of $Gd_{0.49}Sr_{0.51}Fe_{0.79}Co_{0.24}O_{3-\delta}$ (upper) and $Gd_{0.76}Sr_{0.24}Fe_{0.75}Co_{0.22}O_{3-\delta}$ (lower).

vidually was lower than the activity of the composite cathode see Table II. This indicates that the unique microstructure formed when making the composite perovskite is essential for good electrochemical activity of this type of SOFC cathode as it also is suggested (but not verified) in Ref. 7.

Table II. ASR values for the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and the two phases present in the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$. The ASR values are calculated from the EIS measurements using Newman's formula.[12]

Sample	ASR (Ω cm^2 at 800°C)
$Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$	0.025
$Gd_{0.49}Sr_{0.51}Fe_{0.79}Co_{0.24}O_{3-\delta}$ (orthorhombic)	0.41
$Gd_{0.76}Sr_{0.24}Fe_{0.75}Co_{0.22}O_{3-\delta}$ (cubic)	3.33

Conclusion

A candidate cathode for SOFC applications has been produced. It was shown that this cathode consisted of two perovskite phases. The composite cathode was better than the two individual phases separately, indicating that the unique microstructure of the two-phase system is essential for obtaining high electrochemical activity for the reduction of oxygen in a SOFC.

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